

Ammonium Persulphate Initiated Graft Copolymerization of Aniline onto Chitosan-A Comparative Kinetic Study

Seyed Hossein Hosseini

Nika Pooyesh Industrial Research Institute, NBP Economic Group, Tehran, Iran

RESEARCH ARTICLE

ABSTRACT: Ammonium persulphate (APS) has been used as efficient initiator for graft copolymerization of the aniline (ANI) onto chitosan at $25 \pm 0.1^\circ\text{C}$. Graft copolymerization of ANI onto chitosan has taken place through the cation radical initiation process. The grafting parameters have been evaluated by varying concentration of ANI, APS and chitosan. The effects of concentration of APS, ANI, chitosan and reaction time on graft copolymerization were studied by determining the grafting percentage (%G), grafting efficiency (%E) and percentage add-on. It was observed that rate of homopolymerization (R_h) and rate of graft copolymerization (R_g) increased with the increase in concentration of each component. On the basis of the experimental observations, initiating steps have been proposed and a suitable rate expression for graft copolymerization has been derived. Electrical conductivity of grafted polyaniline (PANI) onto chitosan (Chit-g-PANI, chitaline) was measured by the four probe method.

KEYWORDS: graft copolymerization, polyaniline, chitosan, kinetic study

<https://doi.org/10.29294/IJASE.7.4.2021.1975-1982> © 2021 Mahendrapublications.com, All rights reserved

INTRODUCTION

The study of the kinetics and mechanism of different polymerizations is very important for a better understanding of laboratory and industrial products. These studies can be in the field of investigating the kinetics of various polymerizations such as radical [1], cationic [2], anionic [3] or ring-opening [4]. Beers describes how atom transfer radical polymerization (ATRP) into the mechanism and kinetics polymerization process [5]. Graft copolymerization is a useful technique for modifying the properties of the synthetic and natural polymers [6]. Therefore, it is very important to study the kinetics of grafting. In this way, the grafting percentage, reaction rate, reaction efficiency, branch length and molecular mass of the final polymer can be achieved [7]. Application of chitosan grafted materials in biomedical gloves, cosmetic, artificial skin and dressings are very attractive [8]. The high proportion of amino functions in chitosan has been found to provide novel binding properties in hydrogel exhibiting a great potential for burn treatment [9]. Chitosan and its composites are also considered as a good candidate for the drug delivery system [10], enhanced antimicrobial and wound-healing activity [11] and biomedical application [12].

Conducting polymers (CPs) are at the focal point of technology generation and bio-communication materials. These compounds in the form of homopolymers and copolymers are widely used in various medical, military and industrial

applications [13-15]. These polymers are called intelligent polymers and have unique uses in various forms with other compounds as nanocomposites [16]. Preparation and kinetics of graft copolymerization of chitosan and (CPs) were investigated, too [14].

In the preceding works, copolymer of polyaniline grafted on polyvinyl propionate for some of pesticide poisons sensor were reported [18]. In the last work, Chitosan-g-Polyaniline (Chitaline) was carried out by chemical and electrochemically polymerization [19] and Kinetics of copolymerization of 2-anilinoethanol onto chitosan by ammonium peroxydisulfate as initiator was studied, too [20].

In this work, we investigated kinetic behavior of formation of Chitaline. So, the effects of concentration of APS, ANI and the reaction time on graft copolymerization were studied by determining the grafting percentage, grafting efficiency and percentage add-on. In continue we measured the efficiency (%E) and grafting (%G) percentages and electrical conductivities of the graft copolymer. Figure 1 shows all steps of formation of Chitaline.

EXPERIMENTAL

Materials

Chemicals used in this study were American Chemical Society (ACS) grade. The sample of pure chitosan was obtained as a gift from Fluka Chemical Co. Its degree of deacetylation >85% and

*Corresponding Author: dr.shhosseini@gmail.com

Received: 15.03.2021

Accepted: 21.04.2021

Published on: 31.05.2021

Seyed Hossein Hosseini

the molecular weight was 600,000. According to the publications chitosan flakes are being grinded to powders and dried under vacuum at room temperature. Aniline (Merck) was dried with

NaOH, fractionally distilled under reduced pressure from sodium or CaH_2 . Other chemicals and solvents were purified as per standard procedure before use.

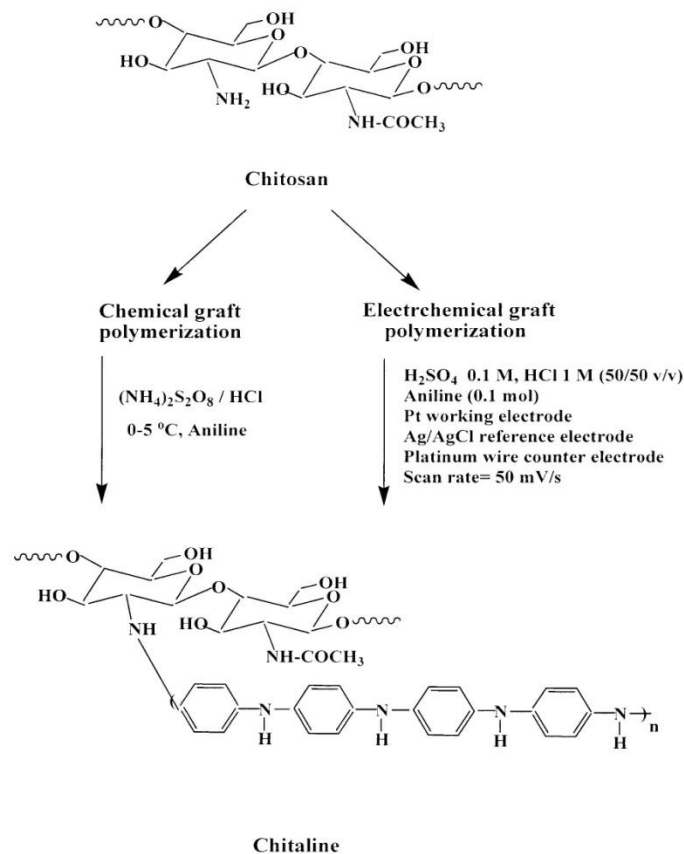


Figure 1. All steps of formation of Chitaline

Chemical synthesis chitosan-polyaniline graft copolymer (Chitaline)

Chemical graft copolymerization was carried out in a 100 mL four-necked flask equipped with thermometer, condenser, stirrer and gas inlet. In a typical reaction, 0.4 g chitosan in 30 mL acetic acid 2% was added with constant stirring under nitrogen and degassed for 1 hrs. The solution from 1.23 g (0.0054 mol) APS in 20 mL acetic acid (2%) was added to flask in 0-5°C. The mixture was kept under N_2 atmosphere, then 0.5 g (0.0054 mol) aniline suspended in 10 mL distilled water and was added dropwise via a syringe through a rubber septum. The solution was reacted at room temperature with magnetic stirring in nitrogen atmosphere. After a further 12 h continuous stirring, the mixture became a black solution. The precipitate obtained was collected by filtration and thoroughly washed with distilled water and

methanol. Dried at 40°C for 24 h under vacuum, a green black powder was obtained.

Electrochemical synthesis chitosan-polyaniline graft copolymer (Chitaline)

Electrochemical polymerization carried out by coating chitosan on surface Pt disk working electrode, then growth PANI onto chitosan in acidic solution. Chit-g-PANI was prepared by applying intended potential to the electrode using potentiostat. In this electrolysis a standard three-electrode cell, without any cell partition, using a Pt working electrode a Pt counter electrode, and Ag/AgCl electrode as a reference electrode was employed. The electrolyte solution consisted of 0.1 M aniline in 20 mL of 50:50 (v/v) mixtures of 0.1 M sulfuric acid and 1 M hydrochloric acid in water. The potential range for electrochemical polymerization and the scan rate were -0.5 to 2 V (versus Ag/AgCl) and 50 mVs^{-1} , respectively.

RESULT AND DISCUSSION

Chemical modifications will open ways to various utilizations of polysaccharides. Of possible modifications, graft copolymerization is anticipated to be quite promising for developing sophisticated functions; it would enable a wide variety of molecular designs to afford novel types of tailored hybrid materials composed of natural polysaccharides and synthetic polymers. Graft copolymerization of synthetic polymers onto chitosan can introduce desired properties and enlarge the field of the potential applications of them by choosing various types of side chains.

Conductivity measurements

The conductivities of PANI, PANI grafted and ungrafted onto chitosan were measured. Table 1 shows the effect of the weight ratio of 93).

Rate measurements

chitosan/aniline on the conductivity. Chitaline showed a good conductivity value better than of pure chitosan and lower than PANI. It is not quite clear how the polymer grafted modifies the conductivity of the polymer. However, besides the chemical structure and chain conformation, there are many factors that may influence the conductivity, such as chain packing and morphology of the polymer. The backbone polymer, chitosan, can be expected to increase the torsional angle between adjacent rings to relieve the steric strain. This may contribute to the lower conductivities of Chitaline as compared to the unsubstituted PANI. It was found that the conductivity values increased with increase in % grafting (Table 1). This confirms the chemical grafting of PANI onto chitosan matrix [20,21]. Conductivity changes were measured with a four-probe device (home-made, ASTM Standards, F 4

The rate of grafting (R_g), rate of homopolymerization (R_h), grafting and efficiency percentages were calculated as follows

$$R_g = \frac{W_3 - W_1}{V \cdot T \cdot M_{\text{ANI}}} \times 1000 \quad \% \text{ grafting} = \frac{W_3 - W_1}{W_1} \times 100$$

$$R_h = \frac{W_2 - W_3}{V \cdot T \cdot M_{\text{ANI}}} \times 1000 \quad \% \text{ efficiency} = \frac{W_2 - W_3}{W_4} \times 100$$

where t =reaction time, M =molecular weight of the monomer and V =total volume of the reaction mixture.

Effect of ANI concentration on R_h and graft parameters

The graft copolymerization has been recorded at different concentrations of [ANI] ranging from 0.1 to 0.4 mol/L at constant concentrations of [APS] (0.2 mol/L) and chitosan (0.1 g) at $25 \pm 0.1^\circ\text{C}$. The effect of varying the [ANI] on R_h and graft parameters such as R_g , %G and %E are presented in Table 2. The R_g at different concentrations of [ANI] has been used to determine the order of reaction by drawing a plot between R_g and concentration of [ANI]. So, effect of [ANI]/chitosan ratio on graft copolymerization of [ANI] onto chitosan is depicted in Figure 2, too. The %G and %E have shown an increase trend with the increasing of [ANI] concentration. In the [ANI] concentration range of 0.1 to 0.4 mol/L, R_h , R_g and other graft parameters value apparently increased as the [ANI] concentration grew because the local [ANI] concentration in or around the soluble chitosan increased. This helped the diffusion of the monomer molecules into the radical centers on the

backbone. The plots of R_h and graft parameters vs. [ANI] are drawn. The plot indicates the first order dependence of R_h and R_g on [ANI] and intercept of the plots R_h and R_g vs. [ANI] were noted.

Effect of APS Concentration on R_h and graft parameters

The graft copolymerization of ANI onto chitosan has been studied at [APS] concentration range 0.5 to 3 mol/L and constant concentrations of [ANI] (0.2 mol/L) and chitosan (0.1 g). The effects of varying the [APS] on R_h and graft parameters are presented in Table 3. Here again the R_h and R_g values showed increasing trend with [APS]. In a separate set of experimental conditions different from the above mentioned conditions, the effect of [APS] on R_h and graft parameters were studied (Figure 3). The increasing trends in grafting parameters have been attributed to the formation of more active sites on chitosan with the increasing concentration of [APS] in the reaction mixture. The produced active sites were consumed

in the formation of grafted chains on chitosan, which is apparent from the increasing trend in the %G and %E magnitudes. In addition, the initiating process for APS in graft copolymerization is similar to that of those common free cation-radical initiators, which first decompose and form free cation-radicals and then these free cation-radicals react with the monomers and start the propagation of the chains. On the other hand, increasing free cation-radicals can increase rate of termination steps, so we can see low molecular weight for copolymer.

The plots of R_h , R_g , %G and %E vs. [APS] were drawn. The R_g calculated at different concentrations of [APS] was used to determine the order of reaction with respect to the concentration of [APS] as shown in Figure 3. In this Figure, there is a linear relation between the rate of graft copolymerization and sub-duplicate concentration of [APS], indicating half order with respect to the concentration of [APS]. This half order dependence of concentration of [APS] has suggested the termination of grafted and ungrafted chains by bi-molecular coupling of two growing chains.

Table 2. Effect of [ANI] on R_h and graft parameters

[ANI] (mol L ⁻¹)	$R_h \times 10^7$ (mol L ⁻¹ S ⁻¹)	$R_g \times 10^7$ (mol L ⁻¹ S ⁻¹)	%Grafting	%Efficiency
0.1	4.2	2.1	11.5	8.5
0.2	8.9	4.0	16.5	12.5
0.3	12.1	6.2	22.4	15.1
0.4	14.2	8.2	24.4	18.9

[APS] = 0.2 mol L⁻¹, HCl = 0.1 M, weight of chitosan = 0.1 g

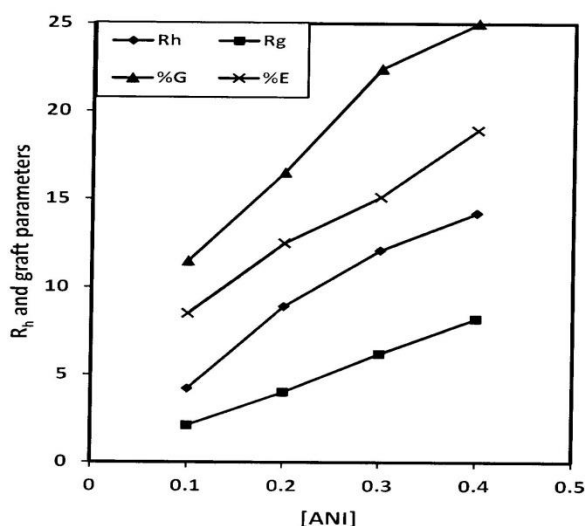


Figure 2. The plots of variation of R_h and graft parameters (R_g , %G, %E) at different [ANI] in presence of fixed of [APS] and [chitosan]

Effect of chitosan concentration

The graft copolymerization of ANI onto chitosan has been carried out at different concentrations of chitosan ranging from 0.075 to 0.30 g but at constant concentrations of [ANI] (0.2 mol/L) and [APS] (0.2 mol/L). The effect of amount of chitosan

on R_h and graft parameters were studied under the conditions mentioned in Table 4. R_h and R_g increased with increase in amount of chitosan. Effect of the concentration of chitosan on %G and %E were plotted in Figure 4. The results show that %G was reduced if the amount of [chitosan] was increased, because the ratio of the [ANI] to

Seyed Hossein Hosseini

[chitosan] was lowered. The slope values of the plots were found to be close to one indicating first order dependence of R_h and R_g on weight of chitosan. These plots were found to be linear and passing through the origin. The linear plots support the clear first order dependence of R_h and R_g on backbone amount. This led to a decrease in the [ANI] concentration in every chitosan molecule, even though the graft rate becomes fast because of the greater number of cation radical centers formed on the backbone as a whole.

Table.3 Effect of [APS] on R_h and graft parameters

[APS] (mol L ⁻¹)	$R_h \times 10^7$ (mol L ⁻¹ S ⁻¹)	$R_g \times 10^7$ (mol L ⁻¹ S ⁻¹)	%Grafting	%Efficiency
0.5	6.3	3.5	9.1	13.1
1	7.6	4.2	13.0	16.5
2	10.2	5.5	18.9	23.1
3	13.4	7.8	23	31.5

[ANI]= 0.2 molL⁻¹, HCl=0.1 M,
weight of chitosan= 0.1 g

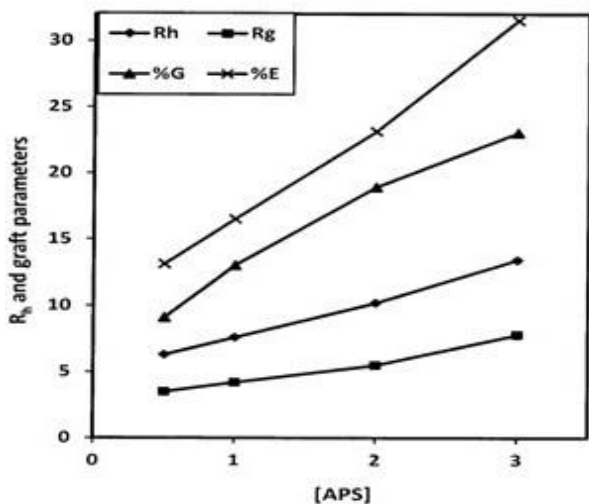


Figure 3. The plots of variation of R_h and graft parameters (R_g , %G, %E) at different [APS] in presence of fixed of [ANI] and [chitosan]

Chemical structures

Cation radical formation on chitosan macromolecules is a key issue in discussing the graft mechanism. The mechanism suggested for

graft copolymerization of PANI onto chitosan in this paper is based on the mechanism proposed by a few research groups [20]. Wang et al [22] explained the formation of homopolymer via cation radical and mechanism for the graft copolymerization of PANI onto various natural polymers by chemical and electrochemical methods. Taking the above mechanisms as basis, a probable mechanism is suggested here to explain the modification of chitosan through chemical grafting. On the basis of the observed experimental data for graft copolymerization of ANI onto chitosan in the presence of APS, the creation of free cation radicals during the graft copolymerization of ANI onto chitosan may be described by the following equations:

Table 4. Effect of [Chitosan] on R_h and graft parameters

[Chitosan] (g)	$R_h \times 10^7$ (mol L ⁻¹ S ⁻¹)	$R_g \times 10^7$ (mol L ⁻¹ S ⁻¹)	%Grafting	%Efficiency
0.075	2.9	1.5	3.8	5.0
0.15	5.6	3.1	6.6	9.8
0.23	7.3	4.6	8.9	13.5
0.30	9.1	5.1	12.5	18.5

[ANI]= 0.2 molL⁻¹, [APS]= 0.2 molL⁻¹, HCl=0.1 M

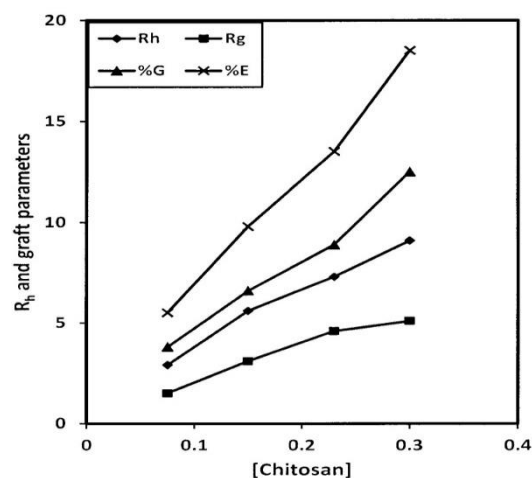
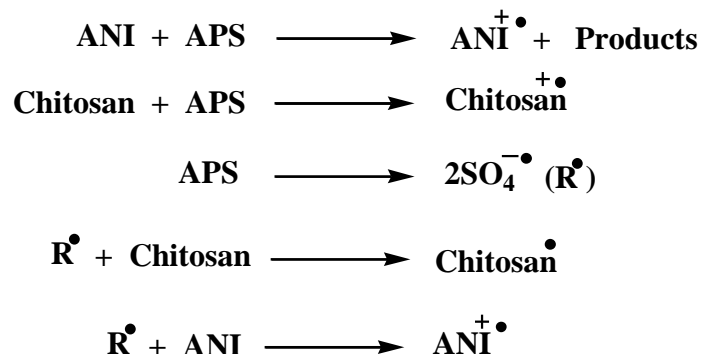
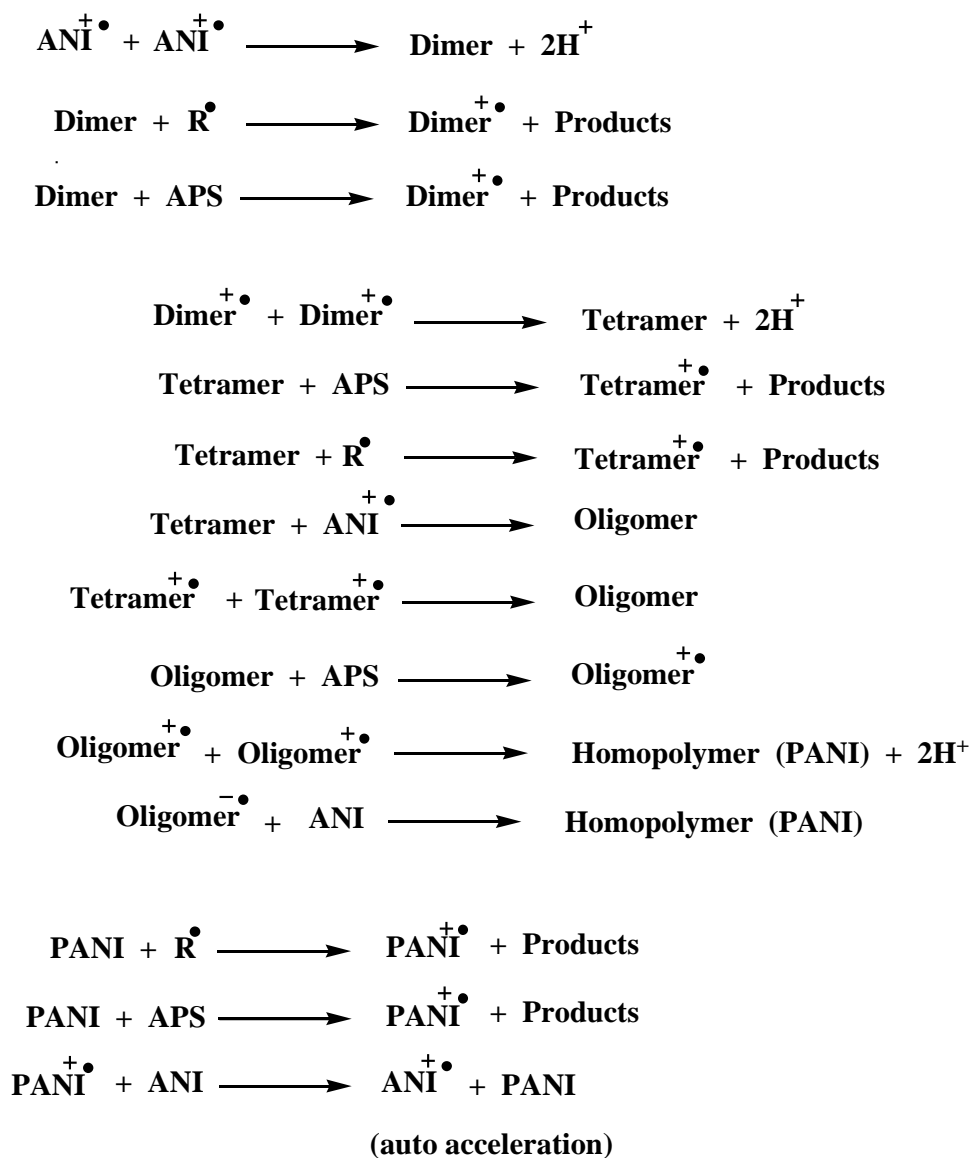
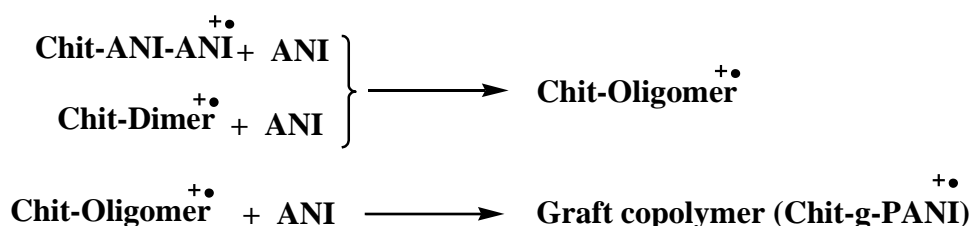
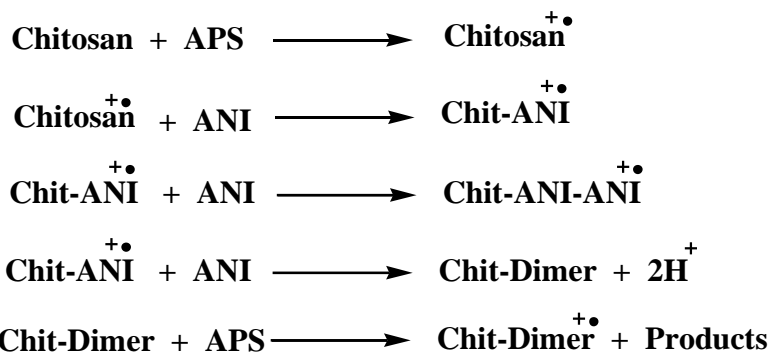


Figure 4. The plots of variation of R_h and graft parameters (R_g , %G, %E) at different [chitosan] in presence of fixed of [ANI] and [APS]

Initiation reactions**Homopolymerization**

Graft copolymerization

In a grafting system of ANI, APS and chitosan, the relation of the rate of grafting (R_g) with the monomer, chitosan and initiator concentrations after calculations of slope of lines from Table 2-4, can be written as

$$R_g \propto [\text{APS}]^{1.66}, R_g \propto [\text{ANI}]^{1.76}, R_g \propto [\text{chitosan}]^{1.08}$$

$$\text{so}; R_g = K[\text{APS}]^{1.66}[\text{ANI}]^{1.76}[\text{chitosan}]^{1.08}$$

CONCLUSION

Graft copolymerization was employed as an important technique to obtain a chemically modified chitosan. The APS has been found to be an efficient initiator for graft copolymerization of ANI onto chitosan in aqueous medium. Percent grafting and efficiency were calculated by gravimetry. The extent of grafting of ANI onto chitosan has shown dependence on concentration of ANI, APS, chitosan and the time reaction of graft copolymerization. There are higher graft percentage and lower homopolymer formation. Free cation-radical formation steps for graft copolymerization were described. The reaction rate for the graft copolymerization of ANI onto chitosan under the initiation of APS was according to the equation of

$$R_g = K[\text{APS}]^{1.66}[\text{ANI}]^{1.76}[\text{chitosan}]^{1.08}.$$

REFERENCES

- [1] Kubisa, P., 2020. Kinetics of radical polymerization in ionic liquids. *European Polymer Journal*, 133, 109778.
- [2] Zhifei, C., Shuxin, L., Yuwei, S., Shan, H., Kangda, W., Wenli, G., Yibo, W., 2020. Cationic Copolymerization of Isobutylene with 4-Vinylbenzenecyclobutylene: Characteristics and Mechanisms. *Polymers*, 12, 201
- [3] Wendel, R., Rosenberg, P., Wilhelm, M., Henning, F., 2020. Anionic Polymerization of ϵ -Caprolactam under the Influence of Water: 2. Kinetic Model. *J. Compos. Sci.* 4, 8.
- [4] Hurst, P. J., Rakowski, A. M., Patterson, J. P., 2020. Ring-opening polymerization-induced crystallization-driven self-assembly of poly-L-lactide-block-polyethylene glycol block copolymers. *Nature Communications*, 11, 4690-4702.
- [5] Beers, K. L., 2020. The first dive into the mechanism and kinetics of ATRP. *Macromolecules* 53, 1115–1118.
- [6] Sharma, G., Kumar, A., Naushad, M., Al-Misned, F. A., El-Serehy, H.A., Ghfar, A. A., Sharma, K. R., Si, C., Stadler, F. G., 2020. Graft Copolymerization of Acrylonitrile and Ethyl Acrylate onto Pinus Roxburghii Wood Surface Enhanced Physicochemical Properties and Antibacterial Activity. *Journal of Chemistry* 2020, 1-16.
- [7] Racovita, S., Baranov, N., Macsim, A. M., Lionte, C., Cheptea, C., Sunel, V., Popa, M., Vasiliu, S., Desbrieres, J., 2020. New Grafted Copolymers Carrying Betaine Units Based on Gellan and N-Vinylimidazole as Precursors for Design of Drug Delivery Systems. *Molecules* 25, 5451.

- [8] Przekora, A., 2020. Review, A Concise Review on Tissue Engineered Artificial Skin Grafts for Chronic Wound Treatment: Can We Reconstruct Functional Skin Tissue In Vitro? Cells 9.
- [9] Dang, L. H., Nguyen, T. H., Tran, H. L. B., Doan, V. N., Tran, N. Q., 2018. Injectable Nanocurcumin-Formulated Chitosan-g-Pluronic Hydrogel Exhibiting a Great Potential for Burn Treatment. J. Healthc. Eng. 2018, 5754890.
- [10] Parhi, R., 2020. Drug delivery applications of chitin and chitosan: a review, Environmental Chemistry Letters 18, 577–594.
- [11] Ye, H., Cheng, J., Yu, K., 2019. In Situ Reduction of Silver Nanoparticles by Gelatin to Obtain Porous Silver Nanoparticle/Chitosan Composites with Enhanced Antimicrobial and Wound-Healing Activity; Elsevier B.V.: Amsterdam, The Netherlands, Volume 121.
- [12] Yuanlan, N., Wen, S., Fen, A., 2020. Application of blocking and immobilization of electrospun fiber in the biomedical field. RSC Adv., 2020, 10, 37246-37265.
- [13] Maity, N., Dawn, A., 2020. Conducting Polymer Grafting: Recent and Key Developments A review. Polymers 12, 709.
- [14] Hosseini, S. H., Azimi, A., Dolabi, M. B., 2020. Study of UV-Visible and near infrared absorption CsXWO₃/polypyrrole nanocomposite. Materials Research Innovations 24, 335-340.
- [15] Dolabi, M. B., Azimi, A., Hosseini, S. H., 2020. Preparation of thermal infrared and microwave absorber using WO₃/MnFe₃O₄/polyaniline nanocomposites. Materials Research Innovations 24, 326-334.
- [16] Hosseini, S. H., Paymanfar, A., Afshari, T., Hosseini, S. S., 2020. Preparation of MWCNT/Ba_{0.2}Sr_{0.2}La_{0.6}MnO₃/PANI nanocomposites and investigation of its electromagnetic properties in KU-band. International Journal of Physical Sciences 15, 171-181.
- [17] Jarosz, T., Gebka, K., Stolarczyk, A., 2019. Recent Advances in Conjugated Graft Copolymers: Approaches and Applications, A review. Molecules 24, 3019.
- [18] Hosseini, S. H., 2013. Studies of Conductivity and Sensing Behavior of Polyaniline Grafted on Polyvinyl propionate for Pesticide Poisons. Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry 43, 852-860.
- [19] Hosseini, S. H., Simiari, J., Farhadpour, B., 2009. Chemical and electrochemical graft copolymerization of aniline onto chitosan. Iranian Polym. J. 18, 3-13.
- [20] Hosseini, S. H., 2015. Kinetics study of copolymerization of 2-anilinoethanol onto chitosan by ammonium peroxydisulfate as a initiator. International Journal of Physical Sciences 10, 142-154.
- [21] Rahman, S. U., Bilal, S., and Ali-Shah, A. H., 2020. Synthesis and Characterization of Polyaniline-Chitosan Patches with Enhanced Stability in Physiological Conditions. Polymers, 12, 2870.
- [22] Wang, L., and Xu, Y., 2006. Graft Copolymerization Kinetics of Ethyl Acrylate onto Hydroxypropyl Methylcellulose Using Potassium Persulphate as Initiator in Aqueous Medium. Iranian Polym. J., 15, 467-475.